Extended Lagrangian Born-Oppenheimer Molecular Dynamics

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Born-Oppenheimer molecular dynamics (BOMD) [1], based on the first principles of quantum mechanics, is currently the gold standard for a large class of atomistic simulations in materials science, chemistry, and molecular biology. Unfortunately, BOMD is often limited by some fundamental problems including a very high computational cost, unbalanced phase space trajectories with unphysical hysteresis effects, numerical instabilities, and a systematic long-term energy drift [2,3]. We have developed an extended Lagrangian BOMD (XL-BOMD) that overcomes some of these fundamental shortcomings [4,5].

The Born-Oppenheimer approximation includes a separation between the nuclear and the electronic degrees of freedom, where the forces acting on the atoms are calculated at the electronic ground state. The force evaluation is computationally very expensive, because of the demanding nonlinear self-consistent field (SCF) optimization of the electronic ground state. The number of SCF iterations necessary to converge the solution dominates the computational cost and may range from ten to hundreds of cycles, depending on the system. To reduce the cost, the electronic solution is propagated between time steps. This means that some combination of the optimized electronic degrees of freedom, $\Psi^{SCF} = \{\psi_n^{SCF}\}$, from previous time steps is used as an initial guess in the SCF optimization,

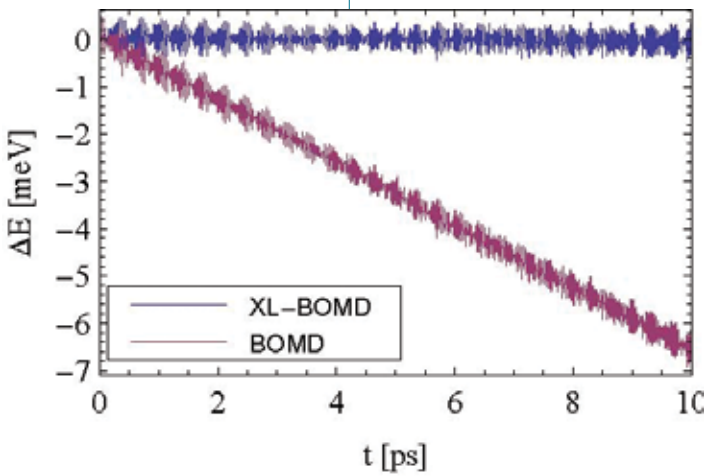

Fig. 1. The fluctuations in total Born-Oppenheimer energy ($\Delta E = E^{tot}(t) - E^{tot}(t_0)$ for a microcanonical eight-atom Si supercell simulation using XL-BOMD and regular BOMD (δt = 1 fs). The implementation was performed in the Vienna ab-initio simulation package (VASP), a plane wave pseudo-potential program for calculations based on Denisty Functional Theory (DFT).

$$\text{i.e.,} \qquad \Psi^{SCF}(t) = \text{SCF}\left[\sum_{n=1}^{N} c_n \Psi^{SCF}(t - n\delta t)\right] \qquad (1)$$

Propagation reduces the number of SCF iterations and thus the computational cost, typically by an order of magnitude, and is necessary for most practical simulations. Unfortunately, evolving the electronic solution through the nonlinear SCF procedure in equation (1) leads to an irreversible propagation, causing unphysical phase space trajectories with a systematic long-term energy drift [2,3]. Only by increasing the degree of SCF convergence, which increases the computational cost, can the systematic errors be reduced though the problems never fully disappear, since the SCF optimization in practice is always incomplete and approximate. Often the unphysical behavior of BOMD is ignored. By using thermostats, e.g., an artificial interaction with an external heat bath, the systematic errors in BOMD are covered up and may never be noticed. However, thermostats require a physically correct underlying dynamics and the errors are therefore never removed.

Our new XL-BOMD solves these fundamental problems by allowing a geometric integration of both the nuclear and the electronic degrees of freedom that preserves geometric properties of the exact flow of the underlying dynamics. This enables highly efficient and accurate long-term microcanonical simulations without a systematic long-term energy drift.

First principles BOMD based on density functional theory (DFT) [1] is given by the Lagrangian:

$$\mathcal{L}^{BO}(\mathbf{R}, \dot{\mathbf{R}}) = \tfrac{1}{2}\sum_i M_i \dot{R}_i^2 - U(\mathbf{R}; \rho^{SCF}) \qquad (2)$$

where $\mathbf{R} = \{Ri\}$ are the nuclear coordinates and the dot denotes the time derivative. The potential $U(\mathbf{R}; \rho^{SCF})$ is the ground state energy including ion-ion repulsions calculated from DFT at the self-consistent electron density given by the wave functions, i.e., $\rho^{SCF} = \sum_n |\psi_n^{SCF}|^2$.

In XL-BOMD [4,5] we extend the dynamical variables of the Born-Oppenheimer Lagrangian with a set of auxiliary wave functions

$\Phi = \{\phi_n\}$ in harmonic oscillators centered around the evolving self-consistent ground state wave functions $\Psi^{SCF}(t)$

$$\mathcal{L}^{XBO}(\dot{\mathbf{R}}, \mathbf{R}, \Phi, \dot{\Phi}) = \mathcal{L}^{BO} + \frac{1}{2}\sum_n \mu_n \int |\dot{\phi}_n|^2 d\mathbf{r} - \frac{1}{2}\sum_n \mu_n \omega_n^2 \int |\psi_n^{SCF} - \phi_n|^2 d\mathbf{r}. \quad (3)$$

Here μ_n and ω_n are fictitious mass and frequency parameters for the harmonic oscillators. The Euler-Lagrange equations of motion in the limit $\mu_n \rightarrow 0$ are given by

$$M_k \ddot{R}_i = -\frac{\partial U(R; \rho^{SCF})}{\partial R_i} \quad (4)$$

$$\ddot{\phi}_n(t) = \omega_n^2 (\psi^{SCF}(t) - \phi_n(t)) \quad (5)$$

The auxiliary wave functions $\Phi(t)$ are dynamical variables and can be integrated by a geometric integration scheme, for example, the time-reversible Verlet algorithm. $\Phi(t)$ will stay close to $\Psi^{SCF}(t)$, since the auxiliary wave-functions evolve in harmonic wells centered around the ground state solutions. Using $\Phi(t)$ as an initial guess in the SCF optimization, therefore provides a very efficient SCF procedure within a framework that can preserve geometric properties of the flow of the underlying dynamics. This is in contrast to the conventional propagation shown in equation (1), where the nonlinear and approximate SCF procedure breaks the time reversibility. Simulations based on XL-BOMD can incorporate time reversibility and other exact properties of the underlying dynamics, even when the force evaluations are based on an incomplete and approximate SCF optimization. This greatly enhances the efficiency and accuracy of MD simulations.

The XL-BOMD approach is quite general and can be used in combination with higher-order symplectic integration schemes, for the propagation of wave functions (as presented here), density matrices [4], effective single-particle Hamiltonians, and the density [6]. In contrast to the popular Car-Parrinello molecular dynamics scheme [1,7], the atomic trajectories evolve on the Born-Oppenheimer potential energy surface with the total self-consistent Born-Oppenheimer energy (kinetic + potential) as the constant of motion. This gives a more accurate dynamics and allows for longer time steps in the integration. Figure 1 illustrates the total energy conservation of XL-BOMD in comparison with regular BOMD with the SCF optimization initialized with a higher-order wave function interpolation from previous time steps. The SCF convergence criteria was the same for the two examples, but the computational cost is lower for XL-BOMD and the systematic energy drift is removed. Figure 2 shows another example implemented in LATTE, a self-consistent tight-binding program developed at LANL [6]. Long-term energy stability is achieved even using only one SCF cycle per time step.

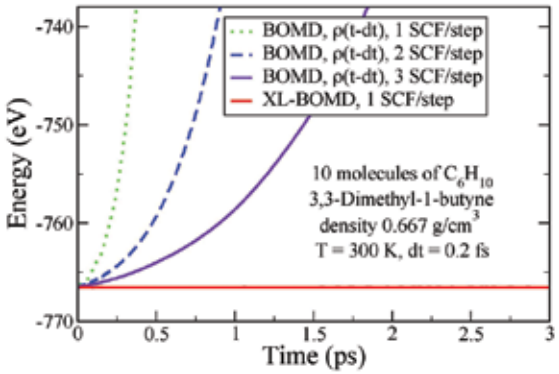

Fig. 2. The total Born-Oppenheimer energy for XL-BOMD and regular BOMD based on a simple propagation of the electronic charge, ρ(t – δt), from the previous time step. The implementation was performed in LATTE [6].

In summary, XL-BOMD provides a new generation of high-performance BOMD within a rigorous and transparent theoretical framework that can combine accuracy and long-term stability with a low computational cost.

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Funding Acknowledgments
LANL Directed Research and Development Program–Exploratory Research (ER)